

Long-lived quasi-stationary coherences in V-type system driven by incoherent light

Timur V. Tscherbul and Paul Brumer

*Chemical Physics Theory Group, Department of Chemistry,
and Center for Quantum Information and Quantum Control,
University of Toronto, Toronto, Ontario, M5S 3H6, Canada**

(Dated: March 27, 2014)

We present a theoretical study of noise-induced quantum coherences in a model three-level V-type system interacting with incoherent radiation, an important prototype for a wide range of physical systems ranging from trapped ions to biomolecules and quantum dots. By solving the quantum optical equations of motion for the V-type system, we obtain analytical expressions for the noise-induced coherences and show that they exhibit an oscillating behavior in the limit of large excited level spacing Δ ($\Delta/\gamma \gg 1$, where γ is the radiative decay rate). Most remarkably, we find that in the opposite limit of small level spacing $\Delta/\gamma \ll 1$, appropriate for large molecules, (a) the coherences can survive for an arbitrarily long time $\tau = (2/\gamma)(\Delta/\gamma)^{-2}$ before eventually decaying to zero, and (b) coherences at short times can be substantial. We further show that the long-lived coherences can be robust against environmental relaxation and decoherence, and discuss implications to the design of quantum heat engines and incoherent light excitation of biological systems.

The dynamics of atomic and molecular systems interacting with noisy electromagnetic fields (such as black-body radiation) is a recurring theme of interest in physics, chemistry, and biology. In particular, the possibility of generating long-lived quantum mechanical coherence via the interaction of multilevel atomic and molecular systems with incoherent light has recently attracted much interest [1–4]. Apart from their fundamental importance, such noise-induced coherences have a wide range of proposed applications, ranging from enhancing the efficiency of photovoltaic devices [1] to lasers without inversion [3] and to the design of artificial light-harvesting antenna complexes [2, 4]. The noise-induced coherences are created via quantum (Fano) interference of the transition amplitudes leading to the same final state—the same process that gives rise to well-known coherent optical phenomena such as coherent population trapping [5], electromagnetically induced transparency [6], vacuum-induced coherence [7, 8], and coherent control [9].

Previous theoretical studies have focused on the production and steady-state properties of noise-induced coherences in atomic Λ and V-type systems [3, 10–13]. For example, Scully and co-workers [3] demonstrated the rich variety and complexity of the steady states reached by the V-type and Λ -type systems interacting with incoherent light, suggested their role in enhancing the efficiency of photosynthetic energy transfer in light-harvesting antenna complexes [2] and suggested possible applications in photovoltaics [1]. However, this and more recent [4] theoretical work focused on the analysis of steady-state properties [1–3, 11] and paid little attention to the time evolution of the coherences. In an earlier contribution, Hegerfeldt and Plenio [12] considered the dynamics of a three-level atomic ion pumped by incoherent radiation and focused on the nature of the emitted light. They demonstrated that in the limit of large excited-state splitting, the intensity correlation function exhibits quantum

beat oscillations due to noise-induced coherences, and in the opposite limit the coherences last longer leading to extended dark periods in the emitted light. However, no closed analytic expressions were derived for the noise-induced coherences, so their time scale and the influence of various system parameters (such as the excited level splitting, and the radiative decay rates) remained unexplored, making it difficult to appreciate and to experimentally observe these coherences in real atomic and molecular systems.

In this Letter, we focus on the dynamical properties of the V-type system, a minimal “building block” for quantum heat engines based on Fano interference [2], crucial to understanding the phenomena of incoherent light excitation in visual phototransduction, solar light harvesting, and photovoltaics. Our analysis is based on a quantum optical master equation of non-Lindblad type [3, 10, 14] that treats all density matrix elements (state populations and coherences) on an equal footing, thereby going beyond the traditional secular approximation. We find analytic expressions for the excited-state populations and coherences in two opposite limits and show that the populations remain positive at all times, thereby demonstrating the existence of positive-definite solutions of a non-Lindblad-type master equation. Our analytic results show that when the energy splitting Δ between the two upper levels of the V-type system is large compared to the radiative decay widths γ , the off-diagonal elements of the density matrix exhibit coherent oscillations that decay on the timescale $\tau_s = 1/\gamma$ (hereafter we set $\hbar = 1$). We further show that in the limit of small energy splitting between excited-state levels ($\Delta \ll \gamma$), (a) short-time coherences are significant, and (b) the coherence between the upper energy levels survives on a timescale $\tau_{\text{long}} = \frac{2}{\gamma}(\Delta/\gamma)^{-2}$ that by far exceeds any other dynamical timescale in the problem (including that of spontaneous decay). This remarkable result suggests that co-

herent dynamics in V-type molecular systems can survive for much longer times *even when* the system is excited by incoherent light (such as sunlight) which has an extremely short correlation time ($\tau_{\text{rad}} = \hbar/kT \sim 1.3$ fs). These results have immediate implications to the design of more efficient quantum heat engines based on Fano interference [1, 2].

To elucidate the time dynamics of the populations and coherences, we solve the Born-Markov quantum optical master equation [16] based on the second-order perturbative expansion of the reduced density operator in the interaction picture:

$$\begin{aligned} \dot{\hat{\rho}}(t) = & -i\text{Tr}_B[\hat{V}(t), \hat{\rho}(t_0) \otimes \hat{\rho}_B(t_0)] \\ & - \text{Tr}_B \int_{t_0}^t [\hat{V}(t), [\hat{V}(t'), \hat{\rho}(t') \otimes \hat{\rho}_B(t_0)]] dt' \end{aligned} \quad (1)$$

where Tr_B denotes the trace over the bath (the incoherent radiation field) with the density operator $\hat{\rho}_B(t_0) = e^{-\beta \hat{H}_B} / \text{Tr}_B e^{-\beta \hat{H}_B}$ assumed to be canonical at all times, $\hat{H}_B = \sum_{\mathbf{k}} \hbar \omega_{\mathbf{k}} \hat{a}_{\mathbf{k}}^\dagger \hat{a}_{\mathbf{k}}$ is the bath Hamiltonian, $\beta = 1/k_B T$ is the inverse temperature of the radiation ($k_B T \sim 0.5$ eV for sunlight with $T = 5800$ K) and $V(t)$ is the atom-field interaction Hamiltonian in the dipole and rotating-wave approximations [3, 14]

$$V(t) = \sum_{i=a,b} \sum_{\mathbf{k}} g_{\mathbf{k}}^{(i)} e^{i(\omega_{ic} - \nu_{\mathbf{k}})t} |i\rangle \langle c| \hat{a}_{\mathbf{k}} + \text{H.c.} \quad (2)$$

Here, $g_{\mathbf{k}}^{(i)} = \boldsymbol{\mu}_{ic} \boldsymbol{\mathcal{E}}_0 / \hbar$ are the coupling constants, $\boldsymbol{\mathcal{E}}_0$ is the electric field amplitude, $\hat{a}_{\mathbf{k}}$ is a destruction operator for a photon mode with wavevector \mathbf{k} and frequency $\nu_{\mathbf{k}}$ [14], $\boldsymbol{\mu}_{ic}$ are the transition dipole moments for the transitions $|c\rangle \leftrightarrow |i\rangle$, and $|i\rangle$, $i = a, b$ denote the excited states of the V-type system [see Fig. 1(a)] coupled by the incoherent radiation to the ground state $|c\rangle$. As typical system-bath couplings for incoherent light excitation of biomolecules are extremely weak, the Born approximation is fully justified [16], as is the Markov approximation, since the coherence time of natural light is extremely short ($\tau_{\text{rad}} = 1.3$ fs for sunlight) [16]. It is thus a good approximation to assume (as we do here) that the correlation function of the incoherent radiation has the form $\langle \mathcal{E}^*(t) \mathcal{E}(t') \rangle = \mathcal{E}_0^2 \delta(t - t')$ [16].

Substituting Eq. (2) into Eq. (1) leads to a system of coupled equations for the density matrix elements in the energy basis [3]

$$\begin{aligned} \dot{\rho}_{aa} = & -(r_a + \gamma_a + \Gamma_a) \rho_{aa} + r_a \rho_{cc} - p(\sqrt{r_a r_b} + \sqrt{\gamma_a \gamma_b}) \rho_{ab}^R \\ \dot{\rho}_{bb} = & -(r_b + \gamma_b + \Gamma_b) \rho_{bb} + r_b \rho_{cc} - p(\sqrt{r_a r_b} + \sqrt{\gamma_a \gamma_b}) \rho_{ab}^R \\ \dot{\rho}_{ab} = & -\frac{1}{2}(r_a + r_b + \gamma_a + \gamma_b + 2\gamma_d) \rho_{ab} - i \rho_{ab} \Delta \\ & + \frac{p}{2} \sqrt{r_a r_b} (2\rho_{cc} - \rho_{aa} - \rho_{bb}) - \frac{p}{2} \sqrt{\gamma_a \gamma_b} (\rho_{aa} + \rho_{bb}). \end{aligned} \quad (3)$$

where $\rho_{ab} = \rho_{ab}^R + i \rho_{ab}^I$, γ_i is the radiative width of level $|i\rangle$, r_i is the incoherent pumping rate, and $p =$

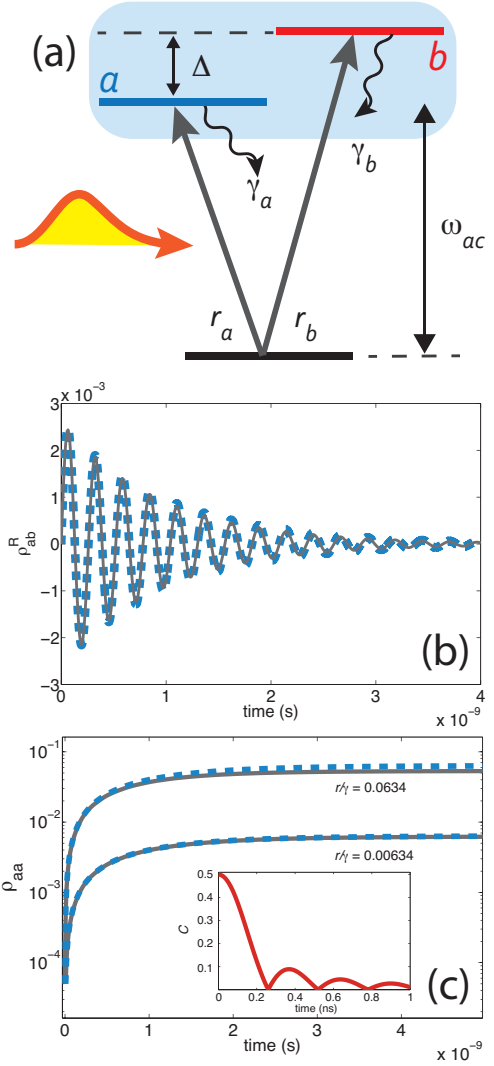


Fig. 1. (a) The energy level structure of the V-type system. The shaded area illustrates the effects of environment-induced relaxation and decoherence on the excited states a and b . The real part of the two-photon coherence $\rho_{ab}^R(t)$ (b) and the population of state a (c). Full lines – exact result (numerical calculations), dashed lines – analytical result obtained in this work in the $\Delta/\gamma \gg 1$ limit ($\Delta = 10^{-4}$ eV, $\gamma = 1$ GHz). The incoherent pumping rate $r/\gamma = \bar{n} = 0.063$ [panels (b) and (c)] and 0.0063 [panel (c)]. $T = 5800$ K and $\omega_{ac} = 1.41$ eV.

$\boldsymbol{\mu}_{ac} \cdot \boldsymbol{\mu}_{bc} / (\mu_{ac} \mu_{bc})$ quantifies the angle between the $c \rightarrow a$ and $c \rightarrow b$ transition dipole moments (hereafter we assume $|p| = 1$). In Eqs. (3), Γ_i are the (phenomenological) relaxation rates, and γ_d is the decoherence rate. For a molecule in the absence of an external environment (the first case considered below), $\Gamma_i = \gamma_d = 0$. Following previous theoretical work [3], we assume that $r_a = r_b = r$, $\gamma_a = \gamma_b = \gamma$. This assumption greatly simplifies the analytical solution of Eqs. (3) while keeping the essential physics of the problem [17]. Imposing the initial conditions appropriate to incoherent excitation of a V-

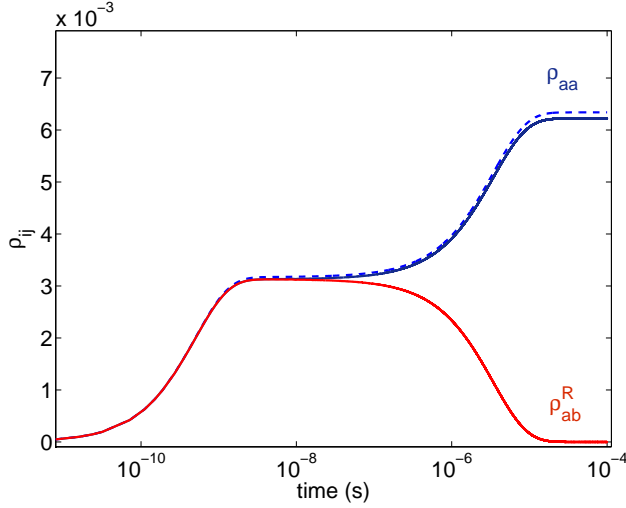


Fig. 2. Excited-state population and coherence dynamics of the V-type system in the $\Delta/\gamma \ll 1$ limit ($\Delta/\gamma = 0.024$, $\Delta = 10^{-7}$ eV, $\gamma = 1$ GHz). Exact results (full line), analytic results (dashed line). The analytic solution for ρ_{ab}^R is virtually indistinguishable from the exact numerical result. Note the quasi-stationary behavior of the coherence over a large time interval, followed by a slow exponential decay. The incoherent pumping rate $r/\gamma = 0.1\bar{n} = 0.0063$.

type system from the ground state, $[\rho_{aa}(0) = \rho_{bb}(0) = \rho_{ab}(0) = 0, \rho_{cc}(0) = 1]$, it is possible to show that Eqs. (3) are equivalent to the following third-order differential equation for the population of state a (all results below are derived in the Supplementary Material [18])

$$\ddot{\rho}_{aa}(t) + a_2\dot{\rho}_{aa}(t) + a_1\rho_{aa}(t) + a_0\rho_{aa}(t) + a = 0 \quad (4)$$

where $a_2 = 5r + 3\gamma$, $a_1 = (r + \gamma)(3r + \gamma) + \Delta^2 + (r + \gamma)^2$, $a_0 = (3r + \gamma)\Delta^2$, and $a = -r\Delta^2$. We note that in deriving Eqs. (3), we do not make the secular approximation, which assumes that the exponential factors $e^{i\omega_{ij}t}$ that enter the equations of motion in the interaction picture [18, 19] average to zero and hence can be neglected. This approximation would separate the time evolution of state populations from that of coherences, leading to the well-known Pauli-type rate equations parametrized by the Einstein coefficients. The secular approximation fails when the system Hamiltonian has quasi-degenerate eigenstates [12, 19], and cannot be justified for a V-type system pumped by incoherent radiation. However, the introduction of non-secular terms means that our equations of motion (3) are no longer of Lindblad type [16], and can therefore have spurious solutions where state populations $\rho_{ii}(t)$ can take unphysical negative values [20]. The use of non-Lindblad-type master equations to describe the quantum dynamics in open systems has been the subject of ongoing debate [4]. Fortunately, as we show in this Letter, the existence of positive solutions is guaranteed for a V-type system subject to initial conditions appropriate to weak-field incoherent excitation.

The solution of Eq. (4) can be represented in the form

$$\rho_{aa}(t) = -a/a_0 + \sum_i \tilde{c}_i e^{\lambda_i t} \quad (5)$$

where λ_i are the roots of the cubic polynomial $\lambda^3 + a_2\lambda^2 + a_1\lambda + a_0 = 0$ to Eq. (4), and \tilde{c}_i are time-independent coefficients to be determined from initial conditions. To obtain the time dynamics of the coherence between the excited-state levels (hereafter referred to as simply “coherence”) we combine Eq. (5) with the expression $\dot{\rho}_{ab}^R = -\frac{1}{p(r+\gamma)}[\dot{\rho}_{aa} + (3r + \gamma + \Gamma)\rho_{aa} - r]$ to find

$$\rho_{ab}^R(t) = -\frac{1}{p(r+\gamma)} \sum_i \tilde{c}_i (3r + \gamma + \lambda_i) e^{\lambda_i t} \quad (6)$$

We note that this solution is *exact*. Quite generally then, the behavior of the coherences in a V-type system is determined by the values of the roots λ_i . A cubic polynomial with real coefficients can have either three real roots (case I) or one real and two complex conjugate roots (case II) [21]. In case I, all λ_i must be negative (for the solutions to be physically sound), and the time dependence of the coherences shows no oscillations, being a sum of decaying exponentials. Alternatively, case II is characterized by a pair of complex eigenvalues, leading to oscillatory coherence dynamics. The latter is qualitatively similar to that previously considered in the framework of semiclassical perturbation theory [23–25]. Below we will show that cases I and II correspond to well-defined physical limits that depend on a single parameter Δ/γ , the ratio of the excited-state level splitting to the decay width.

Consider first the limit of large excited-state splitting, $\Delta/\gamma \gg 1$, applicable to weak-field ($r/\gamma \ll 1$) incoherent excitation [22, 23] of small to medium-sized molecules with typical excited-state lifetimes of 1 – 10 ns (the molecule’s density of states can be no larger than 1 state in $\gamma = 1/\tau \sim 0.005 - 0.05$ cm⁻¹). Under these conditions, the roots of the cubic equation are $\lambda_1 = -\gamma$, $\lambda_{2,3} = -\gamma \pm i\Delta$, and the upper-state population and the real part of the coherence take the form

$$\rho_{aa}(t) = (r/\gamma) [1 - e^{-\gamma t}] \quad (7)$$

$$\rho_{ab}^R(t) = (r/\Delta) e^{-\gamma t} \sin(\Delta t) \quad (\Delta/\gamma \gg 1) \quad (8)$$

with the imaginary part of the coherence $\rho_{ab}^I = (\frac{r}{\Delta}) e^{-\gamma t} [\cos(\Delta t) - 1]$. Figure 1(b) shows that the analytic result (7) is in excellent agreement with the exact time evolution of $\rho_{ab}^R(t)$ obtained by numerical integration of Eq. (3) for $\Delta/\gamma = 40$. The coherence exhibits damped oscillations with frequency Δ and decays to zero on the timescale $\tau_s = 1/\gamma$. Thus, the decoherence timescale in the absence of an external environment other than the incoherent radiation is given by the radiative lifetime of the excited-state levels $\tau_s = 1/\gamma$. On short

timescales ($t \ll \tau_s$), spontaneous decay can be neglected, and the decoherence timescale, quantified by the ratio $\mathcal{C} = |\rho_{ab}^R|/(\rho_{aa} + \rho_{bb})$ [23, 24], decreases as $1/|\Delta t|$ [24]. This dependence reflects the linear growth of excited-state population (Eq. (7) yields $\rho_{aa} = rt$ in the limit $t \ll 1/\gamma$), while the coherences are bounded by r/Δ . The inset of Fig. 1(c) illustrates the slow decrease of $\mathcal{C}(t)$, which is consistent with our previous results obtained independently via a different theoretical approach [15, 23, 24]. However, Eqs. (7) and (8) are required for longer timescales.

In the opposite limit $\Delta/\gamma \ll 1$, which applies to incoherent excitation of a V-type system with very closely spaced upper levels (e.g. a large molecule like Antracene has $\Delta/\gamma \sim 10^{-7}$ [26]), the roots of the cubic equation are given by $\lambda_1 = -2\gamma$, $\lambda_2 = -\gamma$, and $\lambda_3 = -\frac{1}{2}\gamma(\Delta/\gamma)^2$. For the upper-state population and the real part of the coherence we find in the weak pump limit $r/\gamma \ll 1$ (typical values of r/γ for sunlight illumination are on the order of $\sim 10^{-9}$ [22])

$$\rho_{aa}(t) = (r/2\gamma) \left[2 - e^{-2\gamma t} - e^{-\frac{1}{2}\gamma(\Delta/\gamma)^2 t} \right], \quad (9)$$

$$\rho_{ab}^R(t) = (r/2\gamma) \left[e^{-(\gamma/2)(\Delta/\gamma)^2 t} - e^{-2\gamma t} \right]. \quad (10)$$

The imaginary part of the coherence $\rho_{ab}^I = (\frac{r\Delta}{2\gamma^2})[2e^{-\gamma t} - e^{-2\gamma t} - e^{-\frac{1}{2}\gamma(\Delta/\gamma)^2 t}]$ is reduced by the factor $(\Delta/\gamma) \ll 1$. We observe that in the $\Delta/\gamma \rightarrow 0$ limit, the timescale for the decay of the first exponent in Eq. (10), $\tau_{\text{long}} = (2/\gamma)(\Delta/\gamma)^{-2}$ approaches infinity. Thus, Eq. (10) establishes the existence of two widely disparate timescales in coherence dynamics: At shorter times ($t \sim 1/\gamma$), the first exponent on the right-hand side is close to unity, so the coherence grows from zero to a quasi-steady-state value given by $r/2\gamma$. At $t \gg 1/\gamma$ but still short compared to τ_{long} , the coherence remains constant, before eventually decaying to zero at times $t > \tau_{\text{long}}$.

To illustrate this behavior, we provide a log plot in Fig. 2 of the time variation of the population $\rho_{aa}(t)$ and of the coherence ρ_{ab}^R for $\Delta = 10^{-7}$ eV, in the $\Delta/\gamma \ll 1$ limit. The extremely long survival time of the quasi-stationary coherence is apparent: for the given parameters, it survives for as long as 0.1 ms, $> 10^6$ times longer than the excited states' radiative lifetime. This is a consequence of the continuous pumping and the resultant establishment of a quasi-steady state. In the limit of $\Delta \rightarrow 0$, the timescale for the existence of the quasi-stationary coherence approaches infinity, underscoring the crucial role of the excited-state level splitting Δ in determining the noise-induced coherence dynamics. Setting $\Delta = 0$ in Eq. (10) produces a non-zero steady-state value of the coherence $\rho_{ab}^R(\infty) = r/2\gamma$, in agreement with prior $\Delta = 0$ results [3]. However, for any $\Delta > 0$ the coherences have a finite lifetime $\tau_{\text{long}} = (2/\gamma)(\Delta/\gamma)^{-2}$. Maximizing the lifetime of the coherences is beneficial, e.g., to the design of quantum heat engines based on Fano interference

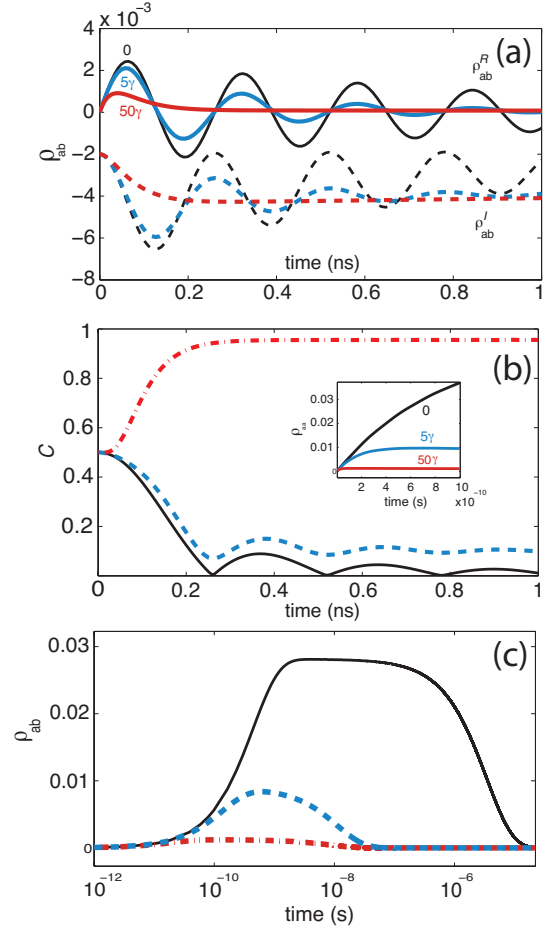


Fig. 3. Effects of environmental relaxation and decoherence on V-type system dynamics: (a) time variation of the real (solid lines) and imaginary (dashed lines) parts of the coherence for $\Delta/\gamma = 24$. The imaginary part of the coherence is shifted down by 0.002 for visual clarity. The values of the decoherence rates (γ_d/γ) are shown next to each curve. (b) The \mathcal{C} -ratio (see text) plotted as a function of time for $\Delta/\gamma = 24$ and $\gamma_d = 0$ (full line), 5 (dashed line), and 50 (dash-dotted line). The inset shows excited-state population dynamics $\rho_{aa}(t)$ for the same values of γ_d . (c) The effect of environmental decoherence on the real part of the coherence for $\Delta/\gamma = 0.024$ (small- Δ limit). In this limit we find that for $\gamma_d \geq 5\gamma$, $\rho_{aa} = \rho_{ab}^R$ and the imaginary part of the coherence is negligible. The relaxation rate $\Gamma = \gamma_d$ in all calculations.

[1, 2], and our analysis suggests the benefit of using as small a Δ as possible.

Both the analytical prediction (10) and the numerical results establish that the time dependence of excited-state populations closely follows that of the coherences up until $t = \tau_s$, thereby implying significant short-time coherence effects, with $\mathcal{C}(t) = 1/2$. This result can also be obtained from a short-time expansion of Eqs. (10), which yields $\rho_{aa} = rt$ and $\rho_{ab}^R = rt$ in the limit $t \ll \tau_s$. We emphasize that this behavior is drastically different from the $1/|t\Delta|$ decay of the coherence-to-population ra-

tio in the limit $\Delta/\gamma \gg 1$ shown in the inset of Fig. 1(c). *This indicates that very closely spaced energy levels undergo radiation-induced decoherence on a much longer timescale than the levels separated by an energy gap that is large compared to their natural linewidth.* Finally, we note that in both small- Δ and large- Δ regimes, the populations $\rho_{ii}(t)$ remain positive at all times, and thus correspond to physical solutions to a non-Lindblad-type quantum optical master equation.

Effects of Relaxation and Decoherence. Thus far we have considered an isolated V-type system (*e.g.* a trapped single ion), for which interaction with environment can be minimized so that the decay rate is solely due to the interaction with the vacuum electromagnetic field. However, the excited states of a V-type system immersed in a condensed-phase environment (*e.g.* a molecule in a liquid) are subject to relaxation and decoherence due to the interaction with the environment. To model these effects, we follow Ref. [1] and explicitly include the relaxation and decoherence terms in the equations of motion via the additional parameters Γ (relaxation rate) and γ_d (decoherence rate).

Figure 3(a) shows the time evolution of the coherence in a V-type system in the limit $\Delta/\gamma \gg 1$. In these calculations, relaxation is assumed to depopulate the excited-state levels with the rate $\Gamma = \gamma_d$, and a modified system of equations (3), augmented with an auxiliary level $|d\rangle$ to collect the population flow from levels $|a\rangle$ and $|b\rangle$, is solved numerically in time. As shown in Fig. 3(a), the value of the decoherence rate γ_d has a major effect on the dynamics, suppressing the coherent oscillations. Already for $\gamma_d = 5\gamma$ [the case shown in Fig. 3(a)], the oscillations are damped on the timescale $\tau_d = 1/\gamma_d$, *i.e.* much sooner than in the absence of environment ($\tau_s = 1/\gamma$). This result suggests that in the regime $\gamma_d \gg \gamma$, the decoherence timescale is set by the environment-induced decoherence, rather than spontaneous decay or relaxation. We note that the asymptotic values of the coherences in the $\Delta/\gamma > 1$ regime can be non-zero even in the presence of rapid decoherence with $\gamma_d = 50\gamma$.

Figure 3(b) illustrates the effect of environmental relaxation and decoherence on the \mathcal{C} -ratio, which quantifies the amount of coherences relative to populations. We observe that for moderate decoherence ($\gamma_d = 5\gamma$) the ratio displays periodic oscillations superimposed on a slowly decaying background. This time dependence is similar to that observed in the absence of relaxation and decoherence, with one important difference: the asymptotic value of \mathcal{C} does not decay to zero due to a finite steady-state value of the coherence shown in Fig. 3(a). This feature becomes even more pronounced as the relaxation and decoherence rates increase; for $\Gamma = \gamma = 50\gamma_d$ the coherences are ~ 9 times large in absolute magnitude than the populations. The origin of this counterintuitive enhancement can be understood by noting that relaxation prevents excited-state population from accumulating by

causing decay to the auxiliary level $|d\rangle$. As shown in the inset of Fig. 3(b), the populations $\rho_{aa}(t)$ tend to saturate at lower steady-state values when relaxation is present, and hence they do not increase as fast as in the relaxation-free regime ($\Gamma = \gamma_d = 0$). While the coherences are also suppressed by environmental decoherence, this effect is not as significant as relaxation-induced suppression of excited-state populations. As a result, the populations can no longer outgrow the coherences and the value of \mathcal{C} saturates at a steady state.

Figure 3(c) illustrates the effects of relaxation and decoherence on quasi-stationary coherences in the $\Delta/\gamma \ll 1$ regime. We observe that relaxation and decoherence lead to a suppression of the coherences, and cause a decrease in the intermediate “plateau” values reached at $t \gg 1/\gamma$. In addition, the *time* at which the plateau is reached decreases with increasing γ_d , suggesting that in the presence of relaxation and decoherence, the dynamics are governed by a timescale $t_d = 1/\gamma_d$ that is shorter than that for spontaneous emission (see Fig. 2). Nevertheless, the coherences are still substantial in absolute magnitude, and the \mathcal{C} -ratio remains close to unity over a large interval of times even in the presence of relaxation.

In summary, we have presented a theoretical analysis of the quantum dynamics of populations and coherences in a V-type molecular system interacting with incoherent radiation, a simple model for a wide array of excitation processes in atomic, molecular, and solid-state systems driven by natural light (such as solar light). We found positive-definite analytical solutions to a non-Lindblad equation of motion for the density matrix and examined them in the limits of large and small excited-state level splittings, compared to the radiative decay width. In the large Δ/γ limit, we find coherent oscillations of excited state coherences, in agreement with recent semiclassical results [23–25]. In the opposite limit of closely spaced excited-state levels, we find unexpectedly long coherence lifetimes. Our results show that the previously studied steady-state coherences in a V-type system [1, 3] have an infinite lifetime *only when* $\Delta = 0$ while in more realistic situations where $\Delta > 0$, the coherences decay on the timescale $\tau_{\text{long}} = (2/\gamma)(\Delta/\gamma)^{-2}$. In either $\Delta/\gamma \gg 1$ or $\Delta/\gamma \ll 1$ regime, the coherences can contribute significantly to the average value of any system property.

We also consider the robustness of these noise-induced coherences against environment-induced relaxation and decoherence. We found that the coherences in the large Δ/γ limit are modified by relaxation, acquiring a non-zero steady-state component. We conclude that in this limit, the decoherence timescale for a molecule embedded in an environment and irradiated with incoherent light is dominated by environmentally-induced decoherence (rather than spontaneous emission). This makes the case of excitation by incoherent light similar to that of molecular excitation by a weak coherent laser source, suggesting the possibility of using incoherent light as a probe

of molecular decoherence mechanisms. Notably, as shown in Fig. 3(b), the population-to coherence ratio does not decrease to zero in the presence of relaxation and decoherence mechanisms, but rather assumes a steady-state value on a timescale $\tau_d \sim 1/\gamma_d$. In the limit of small level spacing ($\Delta/\gamma \ll 1$), the environment tends to suppress the quasi-stationary coherences as shown in Fig. 3(c).

Our work demonstrates that, contrary to expectation, incoherent light excitation can generate long-lived quasi-stationary coherences in atomic and molecular systems. Due to the long lifetime of these noise-induced coherences, it is worthwhile to explore their possible role in biological processes, such as cis-trans photoisomerization of retinal (the first step in vision), or photosynthetic energy transfer. They may also find applications in quantum-enhanced solar energy conversion, and the design of more efficient artificial light-harvesting complexes [2, 4].

We thank Dr. Leonardo Pachón for discussions. This work was supported by NSERC of Canada and by the U.S. Air Force Office of Scientific Research under contract number FA9550-13-1-0005.

-
- * ttscherb@chem.utoronto.ca
- [1] M. O. Scully, K. R. Chapin, K.E. Dorfman, M. B. Kim, and A. Svidzinsky, *Proc. Natl. Acad. Sci. USA* **108**, 15097 (2011).
 - [2] K. E. Dorfman, D. V. Voronine, S. Mukamel, and M. O. Scully, *Proc. Natl. Acad. Sci. USA* **110**, 2746 (2013).
 - [3] V. V. Kozlov, Y. Rostovtsev, and M. O. Scully, *Phys. Rev. A* **74**, 063829 (2006).
 - [4] C. Creatore, M. A. Parker, S. Emmott, and A. W. Chin, *Phys. Rev. Lett.* **111**, 253601 (2013).
 - [5] H. R. Gray, R. M. Whitley, and C. R. Stroud, Jr., *Opt. Lett.* **3**, 218 (1978); J. Vanier, *Appl. Phys. B* **81**, 421 (2005).
 - [6] S. E. Harris, *Phys. Today* **50**, No. 7, 36 (1997).
 - [7] G. S. Agarwal, *Quantum Optics* (Cambridge University Press, Cambridge, UK, 2012), Chap. 17.
 - [8] G. S. Agarwal and K. Patniak, *Phys. Rev. A* **63**, 043805 (2001); E. Paspalakis, S.-Q. Gong, and P. L. Knight, *Opt. Commun.* **152**, 293 (1998).
 - [9] M. Shapiro and P. Brumer, *Quantum Control of Molecular Processes* (Wiley-VCH, Weinheim, 2012).
 - [10] M. Fleischhauer, C. H. Keitel, M. O. Scully, and C. Su, *Opt. Commun.* **87**, 109 (1992).
 - [11] B.-Q. Ou, L.-M. Liang, and C.-Z. Li, *Opt. Commun.* **281**, 4940 (2008).
 - [12] G. C. Hegerfeldt and M. B. Plenio, *Phys. Rev. A* **47**, 2186 (1993).
 - [13] T. P. Altenmüller, *Z. Phys. D* **34**, 157 (1995).
 - [14] M. O. Scully and M. S. Zubairy, *Quantum Optics* (Cambridge University Press, Cambridge, UK, 1997).
 - [15] X.-P. Jiang and P. Brumer, *J. Chem. Phys.* **94**, 5833 (1991); *Chem. Phys. Lett.* **180**, 222 (1991).
 - [16] H.-P. Breuer and F. Petruccione, *The Theory of Open Quantum Systems* (Clarendon Press, Oxford, 2006), Chap. 3.4.
 - [17] We verified by explicit numerical solution of Eqs. (3) that the density matrix dynamics obtained for $r_a \neq r_b$ is very similar to that observed for $r_a = r_b$ provided that the pumping rates are within a factor of 2 of each other.
 - [18] See Supplementary Material for more details concerning the derivation and analytic solution of the equations of motion.
 - [19] C. Cohen-Tannoudji, J. Dupont-Roc, and G. Grynberg, *Atom - Photon Interactions: Basic Process and Applications* (Wiley-VCH, Weinheim, 2004).
 - [20] A. Suárez, R. Silbey, and I. Oppenheim, *J. Chem. Phys.* **97**, 5101 (1992).
 - [21] The exceptional case $\Delta = \gamma$ where the cubic equation has multiple degenerate roots, is unlikely to occur, and will be considered elsewhere.
 - [22] K. Hoki and P. Brumer, *Procedia Chem.* **3**, 122 (2011).
 - [23] Z. S. Sadeq and P. Brumer, *J. Chem. Phys.* **140**, 074104 (2014).
 - [24] T. V. Tscherbul and P. Brumer, *Phys. Rev. A* **89**, 013423 (2014).
 - [25] T. A. Grinev and P. Brumer, to be published.
 - [26] J. Jortner and R. S. Berry, *J. Chem. Phys.* **48**, 2757 (1968).